

# PATENT ABSTRACTS OF JAPAN

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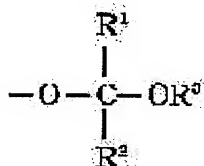
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## (54) BASE RESIN FOR POSITIVE RESIST

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a base resin for a positive resist having high sensitivity and high resolution, excellent in focal depth-width characteristics, shape secular change stability after exposure and the shelf stability of a resist solution and capable of forming a resist pattern excellent in profile shape by using a polyhydroxystyrene having a specified weight average molecular weight and a specified molecular weight distribution.

SOLUTION: The base resin for a positive resist comprises a polyhydroxystyrene having residues of the formula substituted for 10-60 mol% of hydroxyl groups and having a weight average molecular weight of 8,000-25,000 and a molecular weight distribution (Mw/Mn) of  $\leq 1.5$ . In the formula, R<sup>1</sup> is H or methyl, R<sup>2</sup> is methyl or ethyl and R<sup>3</sup> is 1-4C lower alkyl. In the case of <10 mol% substitution rate, a pattern excellent in shape is not obtained. In the case of >60



mol%, the sensitivity of the resist lowers. The substituents are preferably 1-ethoxyethoxy and 1-methoxy-n-propoxy groups because these groups enhance sensitivity and resolving power in a well-balanced state.

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\* NOTICES \*

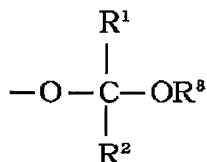
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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

[Claim(s)]

[Claim 1] 10-60-mol% of a hydroxyl group -- the general-formula-izing 1 -- [Formula 1]



(R1 is a hydrogen atom or a methyl group among a formula, R2 is a methyl group or an ethyl group, and R3 is the low-grade alkyl group of carbon numbers 1-4.) Base material resin for positives resist with which it permutes by the residue expressed and 8,000-25,000, and a molecular weight distribution (Mw/Mn) consist [ weight average molecular weight ] of 1.5 or less polyhydroxy styrene.

[Claim 2] (a) Base material resin for positives resist with which the base material resin of claim 1 and 10 - 60-mol% of the (b) hydroxyl group are permuted by the tert-butoxycarbonyloxy radical, and weight average molecular weight is characterized by 8,000-25,000, and a molecular weight distribution (Mw/Mn) consisting of

mixture with 1.5 or less polyhydroxy styrene.

[Claim 3] (a) Base material resin for positives resist according to claim 2 characterized by for a component being 30 - 90 % of the weight, and the (b) component being 10 - 70% of the weight of mixture.

[Claim 4] (a) Base material resin for positives resist according to claim 3 characterized by for a component being 50 - 80 % of the weight, and the (b) component being 20 - 50% of the weight of mixture.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the new base material resin for positives resist used for the positive-resist constituent of the chemistry magnification mold which induces radiations, such as excimer lasers, such as new base material resin for positives resist, ultraviolet rays which can form the resist pattern which does not have a substrate dependency and was excellent in the profile configuration while being high sensitivity and high definition in more detail and excelling in stability with the passage of time and the preservation stability of a resist solution thermal resistance, a depth of focus width-of-face property, and every \*\*, far ultraviolet rays, and KrF, ArF, an X-ray, and an electron ray.

[0002]

[Description of the Prior Art] Conventionally, repetitive manufacturing of the semiconductor devices, such as IC and LSI, is carried out several times in processes, such as photolithography which used the photoresist constituent, etching, impurity diffusion, and wiring formation. In photolithography, after applying a photoresist constituent by rotation spreading etc. on a silicon wafer, forming a thin film, irradiating radiations, such as ultraviolet rays, developing it through a mask pattern and forming a resist pattern, etching is performed by using said resist pattern as a protective coat. Until now, practical use was able to be enough presented with the photoresist constituent currently used with said photolithography by the positive type photoresist to which the definition required of it made the fundamental component the alkali fusibility novolak resin and the quinone diazide radical content compound which are submicron (1 micrometer or less) one and half micron (0.5 micrometers or less) extent, and used ultraviolet rays, such as g line (436nm) and i line (365nm).

[0003] However, detailed-ization of a semiconductor device tends to increase increasingly and the mass production of the VLSI overly using the detailed pattern of a quarter micron (0.25 micrometers or less) tends to start by the end of today in recent years. In the positive type photoresist of such a quarter micron which made the fundamental component conventional alkali fusibility novolak resin and a quinone diazide radical content compound in order overly to have obtained the detailed pattern, development of the resist which used excimer lasers, such as far ultraviolet rays (200-300nm) of short wavelength, and KrF, ArF, the electron ray, and the X-ray more is demanded from the difficult thing. High definition is attained as this resist, upwards, the catalytic reaction of the acid generated by the exposure of a radiation and a chain reaction can be used, the chemistry magnification mold resist which a quantum yield is one or more and can moreover attain high sensitivity attracts attention, and development is performed briskly.

[0004] The resist constituent which combined acid generators which permuted the hydroxyl group of

polyhydroxy styrene by the tert-butoxycarbonyloxy radical, for example, such as a resinous principle and onium salt, as the above-mentioned chemistry magnification mold resist is proposed by the U.S. Pat. No. 4,491,628 number specification.

[0005]

[Problem(s) to be Solved by the Invention] however, the above-mentioned resist constituent be enough upwards in resolution and a depth of focus width of face property, and when a negatives be develop after carry out after [ exposure ] fixed time amount neglect, it have the problem of pattern configuration degradation resulting from deactivation of the acid generated by exposure peculiar to a chemistry magnification mold resist ( henceforth [ every \*\* ] stability ), i.e., the problem of bridging that the resist pattern upper part stand in a row in the shape of eaves. Since a desired circuit pattern will not be obtained if such bridging can be performed, in semiconductor device manufacture, it will become fatal. In order to prevent deactivation of the acid generated by exposure on the resist layer as an approach of solving a problem with the passage of time such every \*\*, there is a method of preparing a topcoat layer, but since a production process increases, a throughput turns up and such an approach serves as cost quantity, it is not desirable. Then, an appearance of the resist which was excellent in stability every [ without the need of preparing a topcoat layer ] \*\* is desired strongly.

[0006] Moreover, the above-mentioned chemistry magnification mold resist has the problem (henceforth a substrate dependency) which serves as a pattern configuration of skirt length to the substrate which prepared insulator layers, such as a silicon nitride (SiN) and boron-Lynn-silicate glass (BPSG), and the film of titanium nitride (TiN).

[0007] Furthermore, when the substrate which prepared metal membranes, such as an alloy of aluminum-silicon-copper (aluminum-Si-Cu) and a tungsten (W), is used, there is a problem from which it is influenced of a standing wave and a pattern cross-section configuration serves as a wave. Although there is a method of preparing an acid-resisting layer between a substrate and a resist layer as an approach of solving these substrate dependencies and troubles of a standing wave, since a production process increases like the above-mentioned topcoat layer, a throughput turns up and this approach serves as cost quantity, it is not desirable. Then, there is no substrate dependency, it is not necessary to prepare an acid-resisting layer upwards, and a resist which can form the resist pattern which was [ that it is hard to be influenced of a standing wave ] excellent in the profile configuration is desired strongly.

[0008] When sufficient resistance turns [ in addition to the above-mentioned trouble ] up to heat as for the conventional resist constituent and it is made into a solution, there is a trouble that preservation stability -- a foreign matter is often generated during the preservation -- is missing. Therefore, while excelling in thermal resistance, to be the resist constituent with which the resist solution excellent in preservation stability without generating of said foreign matter is obtained is also demanded.

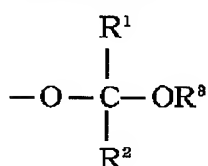
[0009] As a result of this invention person's etc. repeating research wholeheartedly in view of such the present condition, the above-mentioned trouble as a base material resinous principle for positives resist to which the solubility over an alkali water solution increases according to an operation of the (A) acid By using the new polyhydroxy styrene which the specific rate of a hydroxyl group is permuted by the specific substituent, and has specific weight average molecular weight and a specific molecular weight distribution Are solvable by using mixture with the polyhydroxy styrene which the specific rate of a hydroxyl group is permuted by this,

said substituent, and different substituent, and has specific weight average molecular weight and a specific molecular weight distribution. Or by high sensitivity and high definition And while excelling in stability with the passage of time and the preservation stability of a resist solution thermal resistance, a depth of focus width-of-face property, and every \*\* The resist pattern which does not have a substrate dependency and was excellent in the profile configuration can be formed. A header and this invention are completed for the positive-resist constituent of the chemistry magnification mold which induces radiations, such as excimer lasers, such as ultraviolet rays, far ultraviolet rays, and KrF, ArF, an X-ray, and an electron ray, being obtained. Namely, [0010] This invention aims at offering the new base material resin for positives resist.

[0011]

[Means for Solving the Problem] For this invention which attains the above-mentioned purpose, 10 - 60-mol% of the (a) hydroxyl group is the general formula-ization 2 [0012].

[Formula 2]



(-- R1 is a hydrogen atom or a methyl group among a formula, R2 is a methyl group or an ethyl group, and R3 is the low-grade alkyl group of carbon numbers 1-4.) -- it permutes by the residue expressed and 8,000-25,000, and a molecular weight distribution (Mw/Mn) require weight average molecular weight for the base material resin for positives resist which consists of 1.5 or less polyhydroxy styrene.

[0013] the residue to which the base material resin for positives resist of this invention (a) is expressed with the general formula-ization 2 as above-mentioned -- 10 - 60-mol% of a hydroxyl group -- it permutes 20 - 50-mol% of preferably, and weight average molecular weight is [ 8,000-25,000, and a molecular weight distribution (Mw/Mn) ] 1.5 or less new polyhydroxy styrene. Since the sensibility of a resist will fall if the pattern with which the substitutional rate of this polyhydroxy styrene excelled [ less than / 10 mol % ] in the configuration is not obtained but 60-mol % is exceeded, it is effective practical [ 20-50 mol% of ] preferably. As an example of said substituent, for example A 1-methoxyethoxy radical, a 1-ethoxy ethoxy radical, A 1-n-propoxyethoxy radical, 1-isopropoxy ethoxy radical, a 1-n-butoxyethoxy radical, A 1-iso butoxyethoxy radical, 1 -(1 and 1-dimethylethoxy)- 1-methylethoxy radical, A 1-methoxy-1-methylethoxy radical, a 1-ethoxy-1-methylethoxy radical, a 1-n-propoxy-1-methylethoxy radical, a 1-iso butoxy-1-methylethoxy radical, a 1-methoxy-n-propoxy group, a 1-ethoxy-n-propoxy group, etc. are mentioned. Especially, since sensibility and resolving power of a 1-methoxy-n-propoxy group [ a 1-ethoxy ethoxy radical and ] improve with sufficient balance especially, it is desirable. This base material resin (a) can manufacture the hydroxyl group of the polyhydroxy styrene which has the above-mentioned weight average molecular weight and the above-mentioned molecular weight distribution by for example, 1-chloro-1-ethoxy ethane, 1-chloro-1-methoxypropane, etc. in permuting by the residue of said general-formula-izing 2 according to a well-known substitution reaction.

[0014] the above-mentioned base material resin (a) -- 10 - 60-mol% of the (b) hydroxyl group -- it excels [ in definition, thermal resistance, and a profile configuration ] more and is desirable, when it permutes by the

tert-butoxycarbonyloxy radical 20 - 50-mol% of preferably, and weight average molecular weight uses as mixture with 1.5 or less polyhydroxy styrene and 8,000-25,000, and a molecular weight distribution (Mw/Mn) use as a (A) component of a positive-resist constituent. The positive-resist constituent which can form the resist pattern which were high sensitivity and high definition, and does not have a substrate dependency and excelled [ blend / with this (A) component / the compound (henceforth an acid generator) and (C) organic carboxylic-acid compound which generate an acid by the exposure of the (B) radiation ] in the profile configuration while excelling in stability with the passage of time and the preservation stability of a resist solution thermal resistance, a depth of focus width-of-face property, and every \*\* is obtained. The aforementioned (b) component permutes the hydroxyl group of the polyhydroxy styrene which has the above-mentioned weight average molecular weight and the above-mentioned molecular weight distribution by the tert-butoxycarbonyloxy radical for example, by G tert-butyl-G carbonate etc. according to a well-known substitution reaction, and is manufactured. Since sensibility will fall if the resist pattern the substitutional rate of the aforementioned (b) component excelled [ resist pattern ] in the profile configuration less than [ 10 mol % ] is not obtained and 60-mol % is exceeded, 20 - 50-mol % is effective practically preferably.

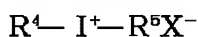
[0015] The 50 - (b) component has [ the 30 - (b) component / the (a) component ] 20 - 50% of the weight of the range preferably good [ the mixed rate of the above-mentioned mixture / the (a) component ] 80% of the weight 90% of the weight ten to 70% of the weight.

[0016] Moreover, based on the gel-permeation-chromatography method (the GPC method), the range of the weight average molecular weight of the above-mentioned (a) component and the (b) component is 8,000-25,000 on polystyrene criteria. When coat nature of weight average molecular weight is not good in the less than 8,000 range and it exceeds the range of 25,000, the solubility over an alkali water solution is inferior. Furthermore, the molecular weight distribution (Mw/Mn) expressed with the ratio of weight average molecular weight (Mw) and number average molecular weight (Mn) need that it is 1.5 or less range. When molecular weight distribution are in said range, thermal resistance improves much more. [0017] As the above-mentioned (B) component, the thing better known than before as an acid generator can be used. There is especially no limit. Specifically (a) bis(p-tosyl) diazomethane, Methyl sulfonyl-p-tosyl diazomethane, 1-cyclohexyl sulfonyl-1-(1 and 1-dimethyl ethyl sulfonyl) diazomethane, Bis(1 and 1-dimethyl ethyl sulfonyl) diazomethane, bis(1-methylethyl sulfonyl) diazomethane, Bis(cyclohexyl sulfonyl) diazomethane, bis(2, 4-dimethylphenyl sulfonyl) diazomethane, Bis(4-ethyl phenyl sulfonyl) diazomethane, bis(3-methylphenyl sulfonyl) diazomethane, Bis(4-methoxyphenyl sulfonyl) diazomethane, bis(4-fluoro phenyl sulfonyl) diazomethane, Bis-sulfonyl diazomethanes, such as bis(4-chlorophenyl sulfonyl) diazomethane and bis(4-tert-buthylphenyl sulfonyl) diazomethane (b) 2-methyl-2-(p-tosyl) propiophenone, A 2-(cyclohexyl carbonyl)-2-(p-tosyl) propane, 2-methane sulfonyl-2-methyl-(4-methylthio) propiophenone, Sulfonyl carbonyl alkanes, such as 2 and 4-dimethyl-2-(p-tosyl) pentane-3-ON (c) 1-p-tosyl-1-cyclohexyl carbonyl diazomethane, 1 - Diazo-1-methyl sulfonyl-4-phenyl-2-butanone, 1-cyclohexyl sulfonyl-1-cyclohexyl carbonyl diazomethane, The 1-diazo-1-cyclohexyl sulfonyl -3, 3-dimethyl-2-butanone, 1-diazo-1-(1 and 1-dimethyl ethyl sulfonyl)-3 and 3-dimethyl-2-butanone, 1-acetyl-1-(1-methylethyl sulfonyl) diazomethane, 1-diazo-1-(p-tosyl)-3 and 3-dimethyl-2-butanone, 1-diazo-1-benzenesulphonyl -3, 3-dimethyl-2-butanone, 1-diazo - 1 -(p-tosyl)-3-methyl-2-butanone, 2-diazo-2-(p-tosyl) cyclohexyl acetate, 2-diazo-2-benzenesulphonyl acetic-acid tert-butyl, 2-diazo-2-methane sulfonyl isopropyl acetate, Sulfonyl carbonyl diazomethanes, such as

2-diazo-2-benzenesulphonyl cyclohexyl acetate and 2-diazo-2-(p-tosyl) acetic-acid tert-butyl (d) P-toluenesulfonic-acid 2-nitrobenzyl, p-toluenesulfonic acid 2, 6-dinitro benzyl, Nitrobenzyl derivatives, such as p-trifluoromethyl benzenesulfonic acid 2 and 4-dinitro benzyl, (e) Methansulfonic acid ester of pyrogallol (pyrogalloltrimesylate), The benzenesulfonic acid ester of pyrogallol, the p-toluenesulfonic-acid ester of pyrogallol, p-methoxybenzene sulfonate of pyrogallol, the mesitylene sulfonate of pyrogallol, The benzyl sulfonate of pyrogallol, the methansulfonic acid ester of gallic-acid alkyl, The benzenesulfonic acid ester of gallic-acid alkyl, the p-toluenesulfonic-acid ester of gallic-acid alkyl, p-methoxybenzene sulfonate of gallic-acid alkyl, the mesitylene sulfonate of gallic-acid alkyl, The polyhydroxy compound, the aliphatic series, or the aromatic series sulfonates of gallic-acid alkyl, such as a benzyl sulfonate, etc. can be mentioned. The alkyl group in said gallic-acid alkyl has desirable alkyl group especially octyl radical, and lauryl radical of carbon numbers 1-15. moreover, (f) -- the onium salt system acid generator expressed with the following general-formula-izing 3 and \*\* 4 and the benzoin TORESHITO system acid generator expressed with (g) general formula-ization 5 can also be used.

[0018]

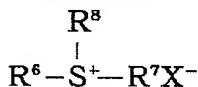
[Formula 3]



(R4 and R5 are aryl groups which have an aryl group and a substituent, it may be the same respectively, or you may differ, and X- is AsF-6, PF-6, BF-4SbF-6, or CF3SO-3.)

[0019]

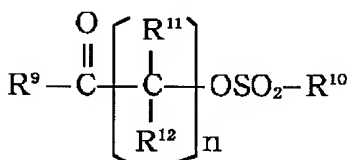
[Formula 4]



(R6, R7, and R8 are aryl groups which have an aryl group and a substituent, it may be the same respectively, or you may differ, and X- is AsF-6, PF-6, BF-4SbF-6, or CF3SO-3.)

[0020]

[Formula 5]

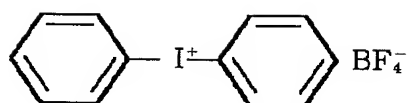


(R9 and R10 are ARURU radicals which have an aryl group and a substituent, even if the same, you may differ, and R11 and R12 are a hydrogen atom, a low-grade alkyl group, a hydroxyl group, and an aryl group, they may be the same or may differ.) n is 0 or 1.

[0021] As a concrete thing of onium salt expressed with the above-mentioned general formula-ization 3 and 4, the compound of following \*\* 6-27 is mentioned.

[0022]

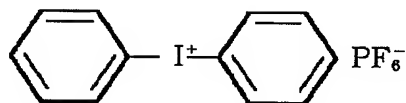
[Formula 6]



ジフェニルヨードニウムテトラフルオロボレート

[0023]

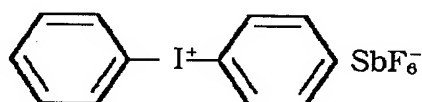
[Formula 7]



ジフェニルヨードニウムヘキサフルオロフォスフェート

[0024]

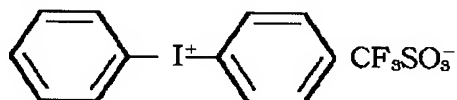
[Formula 8]



ジフェニルヨードニウムヘキサフルオロアンチモネート

[0025]

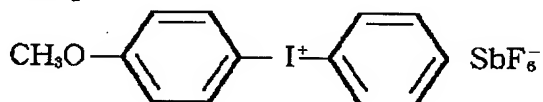
[Formula 9]



ジフェニルヨードニウムトリフルオロメタンスルホネート

[0026]

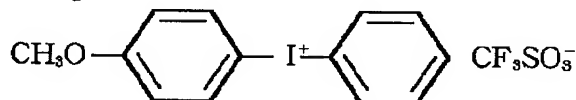
[Formula 10]



(4-メトキシフェニル) フェニルヨードニウムヘキサフルオロアンチモネート

[0027]

[Formula 11]

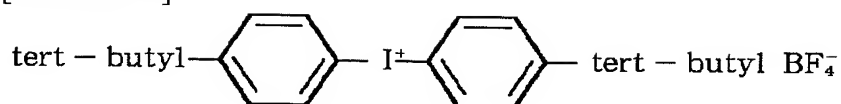


(4-メトキシフェニル) フェニルヨードニウムトリフルオロメタンスルホネート



[0028]

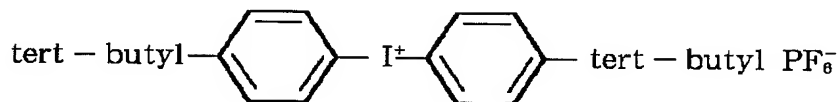
[Formula 12]



ビス (p-tert-ブチルフェニル) ヨードニウムテトラフルオロボレート

[0029]

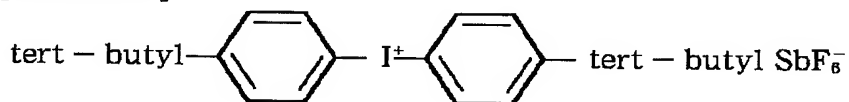
[Formula 13]



ビス (p-tert-ブチルフェニル) ヨードニウムヘキサフルオロフォスフェート

[0030]

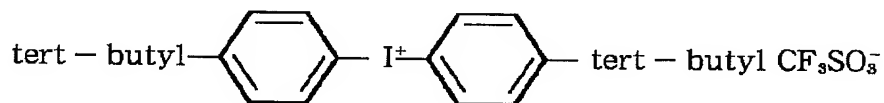
[Formula 14]



ビス (p-tert-ブチルフェニル) ヨードニウムヘキサフルオロアンチモネート

[0031]

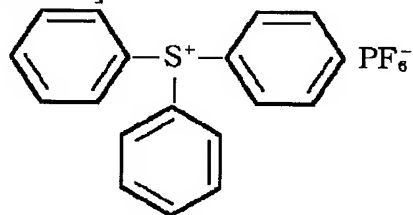
[Formula 15]



ビス (p-tert-ブチルフェニル) ヨードニウムトリフルオロメタンスルホネート

[0032]

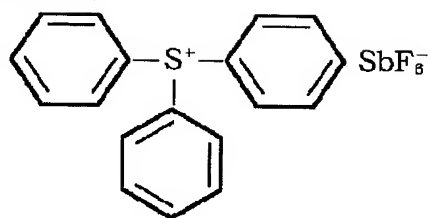
[Formula 16]



トリフェニルスルホニウムヘキサフルオロフォスフェート

[0033]

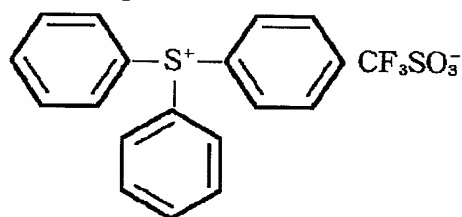
[Formula 17]



トリフェニルスルホニウムヘキサフルオロ  
アンチモネート

[0034]

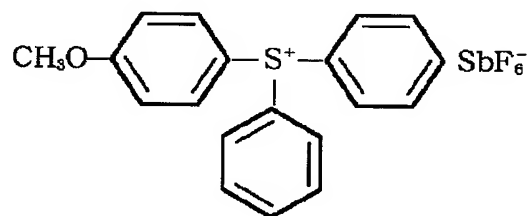
[Formula 18]



トリフェニルスルホニウムトリフルオロメタン  
スルホネート

[0035]

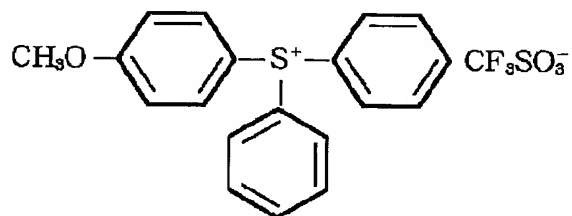
[Formula 19]



(4-メトキシフェニル) ジフェニルスルホニウムヘキサフルオロ  
アンチモネート

[0036]

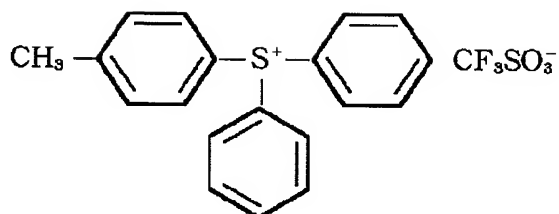
[Formula 20]



(4-メトキシフェニル) ジフェニルスルホニウムトリフルオロ  
メタンスルホネート

[0037]

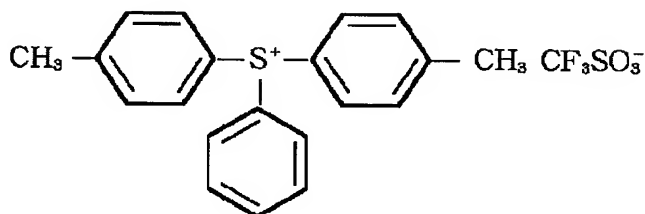
[Formula 21]



(4-メチルフェニル) ジフェニルスルホニウムトリフルオロ  
メタンスルホネート

[0038]

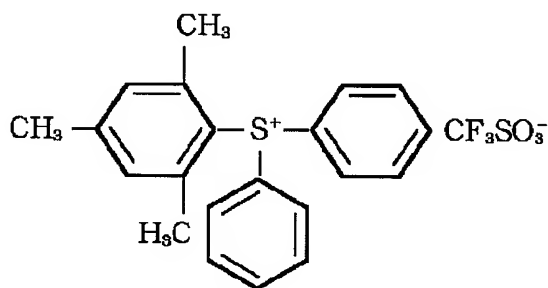
[Formula 22]



ビス (4-メチルフェニル) フェニルスルホニウムトリフルオロ  
メタンスルホネート

[0039]

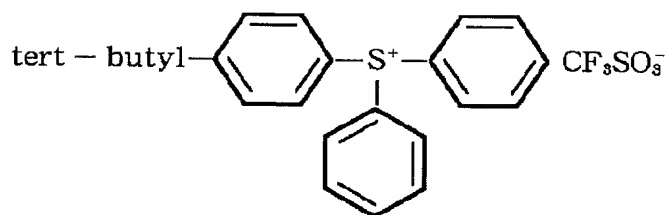
[Formula 23]



(2, 4, 6-トリメチルフェニル) ジフェニルスルホニウムトリフルオロ  
メタンスルホネート

[0040]

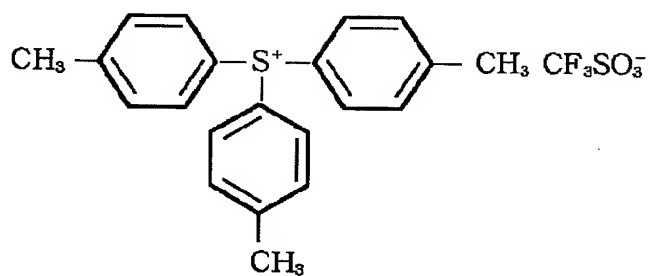
[Formula 24]



(4-tert-butyl-フェニル) ジフェニルスルホニウムトリフルオロメタン  
スルホネート

[0041]

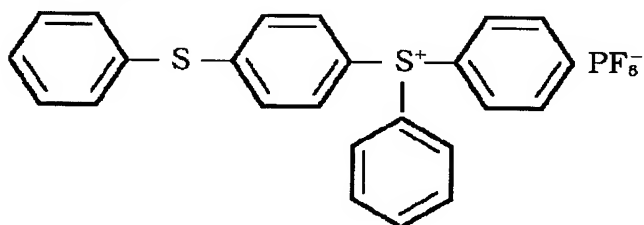
[Formula 25]



トリス (4-メチルフェニル) スルホニウムトリフルオロメタン  
スルホネート

[0042]

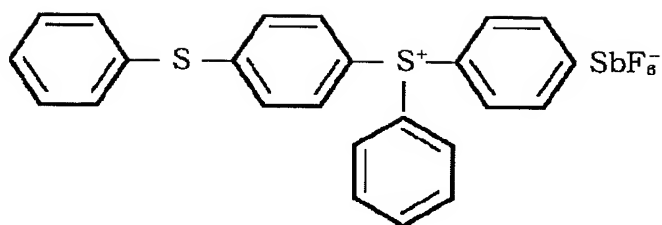
[Formula 26]



ジフェニル [4-(フェニルチオ)フェニル] スルホニウム  
ヘキサフルオロフォスフェート

[0043]

[Formula 27]



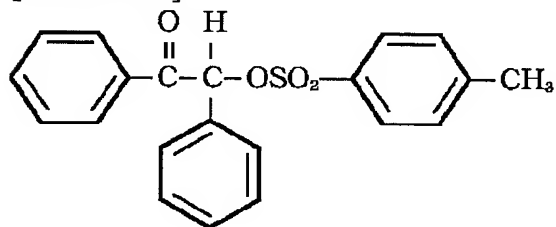
ジフェニル [4- (フェニルチオ) フェニル] スルホニウム  
ヘキサフルオロアンチモネート

[0044] Since the atom used as dispersing agents, such as Lynn used in case the onium salt which uses trifluoromethane sulfonate as an anion in the above-mentioned onium salt is semiconductor device manufacture, boron, and antimony, is not included, it is desirable.

[0045] (g) As a concrete thing of a benzoin tosylate system acid generator, the compound of following \*\* 28-32 is mentioned.

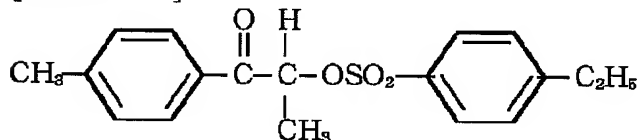
[0046]

[Formula 28]



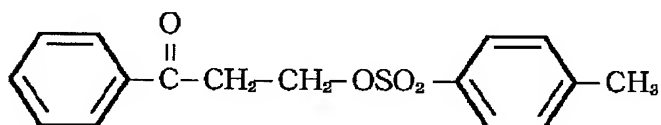
[0047]

[Formula 29]



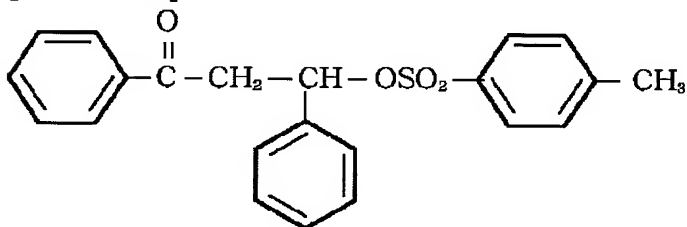
[0048]

[Formula 30]



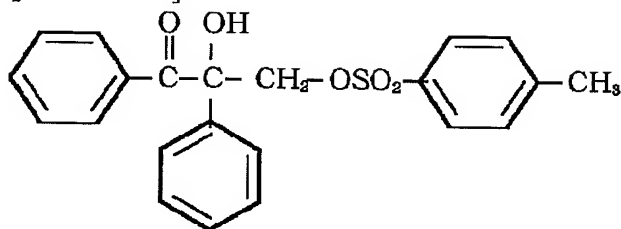
[0049]

[Formula 31]



[0050]

[Formula 32]



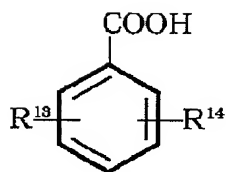
[0051] The above-mentioned acid generator may use one sort, and may use it combining two or more sorts. As a thing suitable in said acid generator for the resist for excimer laser, pyrogalloltrimesylate is good, and especially the mixture of these acid generators can attain high sensitivity, and is desirable also in the aliphatic series of the bis-sulfonyl diazomethanes of (a), inside, bis(cyclohexyl sulfonyl) diazomethane or bis(2, 4-dimethylphenyl sulfonyl) diazomethane, or the polyhydroxy compound of (e), or aromatic series sulfonates.

[0052] Moreover, as a resist system acid generator for electron rays, bis(p-tert-buthylphenyl) iodonium trifluoromethane sulfonate, triphenylsulfonium trifluoromethane sulfonate, and the benzoin TORESHITO system acid generator of (g) are desirable also in the aliphatic series of the nitrobenzyl derivative of (d), inside or p-toluenesulfonic acid 2, 6-dinitro benzyl, and the polyhydroxy compound of (e) or aromatic series sulfonates, inside or pyrogalloltrimesylate, and the onium salt system acid generator of (f). the loadings of said acid generator -- the base material resinous principle 100 weight section for positives resist -- receiving -- 1 - 20 weight section -- the rate of 2 - 10 weight section is preferably good. If the acid generator of effectiveness is inadequate and exceeds 20 weight sections in combination of under 1 weight section, it will melt into a solvent, and will not go out upwards, and a miscibility with many resinous principles will worsen.

[0053] Furthermore, when a positive-resist constituent contains the (C) component, while stability with the passage of time is excellent every \*\* after sensibility, resolution, the cross-section configuration of a resist pattern, and exposure, the resist which forms a resist pattern with a good cross-section configuration also to various substrates is obtained.

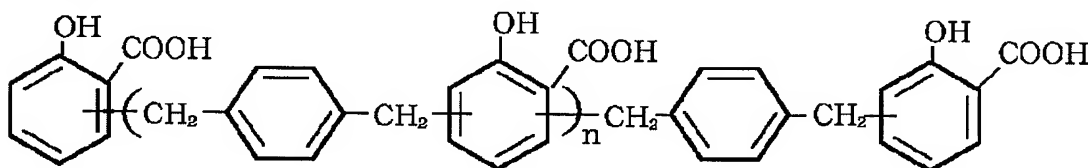
[0054] It is not what all can use saturation or partial saturation aliphatic carboxylic acid, an alicyclic carboxylic acid, hydroxy acid, an alkoxy carboxylic acid, a keto carboxylic acid, aromatic carboxylic acid, etc., and is especially limited as the above-mentioned (C) component. For example, a formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, oxalic acid, a malonic acid, Univalent or multiple-valued aliphatic carboxylic acid of a succinic acid, a glutaric acid, an adipic acid, etc., 1 and 1-cyclohexane dicarboxylic acid, 1, 2-cyclohexane dicarboxylic acid, 1, 3-cyclohexane dicarboxylic acid, 1, 4-cyclohexane dicarboxylic acid, Alicyclic carboxylic acids, such as 1 and 1-cyclo HEKISHIRUJI acetic acid, an acrylic acid, A crotonic acid, isocrotonic acid, 3-butene acid, a methacrylic acid, 4-pentene acid, Partial saturation aliphatic carboxylic acid, such as a PUROPI all acid, a 2-butine acid, a maleic acid, a fumaric acid, and an acetylene carboxylic acid, Keto carboxylic acids, such as alkoxy carboxylic acids, such as hydroxy acid, such as an oxy-acetic acid, a methoxy acetic acid, and an ethoxy acetic acid, and a pyruvic acid, and general-formula-izing 33 [0055]

[Formula 33]



[-- R13 and R14 express independently a hydrogen atom, a hydroxyl group, a nitro group, a carboxyl group, and a vinyl group among a formula, respectively (however, when both R13 and R14 are hydrogen atoms, it removes.).] And general-formula-izing 34 [0056]

[Formula 34]



Although the aromatic carboxylic acid expressed with [n shows the integer of 0, or 1-10 among a formula] can mention, an alicyclic carboxylic acid, partial saturation aliphatic carboxylic acid, and aromatic carboxylic acid are used especially preferably.

[0057] As aromatic carboxylic acid expressed with the above-mentioned general formula-ization 33 For example, para hydroxybenzoic acid, o-hydroxybenzoic acid, a 2-hydroxy-3-nitro benzoic acid, 3, 5-dinitro benzoic acid, 2-nitro benzoic acid, 2, 4-dihydroxybenzoic acid, 2, 5-dihydroxybenzoic acid, 2, 6-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3, 5-dihydroxybenzoic acid, 2-vinyl benzoic acid, 4-vinyl benzoic acid, The benzoic acid which can mention a phthalic acid, a terephthalic acid, isophthalic acid, etc., and especially has a substituent at least in o-, for example, o-hydroxybenzoic acid, o-nitro benzoic acid, a phthalic acid, etc. are suitable.

[0058] Moreover, although it can be used as an aromatic-carboxylic-acid compound expressed with the general formula-ization 34 even if n in a formula combines a thing of a different kind only for a single thing, SAX (a trade name, Mitsui Toatsu Chemicals, Inc. make) marketed as a phenolic compound practical is used preferably.

[0059] The aromatic-carboxylic-acid compound expressed with the above-mentioned general-formula-izing 33 and \*\* 34 may be independent respectively, or two or more sorts may be mixed and used for it. While being able to form a resist pattern with a good cross-section configuration by combination of these aromatic-carboxylic-acid compounds, since the aromatic-carboxylic-acid compound which stability with the passage of time is excellent in every \*\* after exposure, can form a good profile configuration regardless of the die length of the time amount to the heat-treatment performed after exposure, and is expressed especially with the general formula-ization 34 can form a rectangular cross-section configuration, it is suitable.

[0060] (C) As loadings of a component, it is preferably used in 0.05 - 0.5% of the weight of the range 0.01 to 1% of the weight to the total quantity of the (A) component and the (B) component. Since development nature will fall if a resist pattern with a cross-section configuration good at less than 0.01 % of the weight is not obtained for the loadings of an organic carboxylic-acid compound and it exceeds 1 % of the weight, it is not desirable.

[0061] The positive-resist constituent containing the above-mentioned (A) component, the (B) component, and the (C) component can contain preferably resolution and the (D) amine which can raise stability with the passage of time every \*\* in 0.05 - 0.5% of the weight of the range 0.01 to 1% of the weight to the (A) component while it can prevent the diffusion beyond the need for the acid generated by the exposure of a radiation and can form a resist pattern faithful to a mask pattern. As the aforementioned (D) component, fatty amine, aromatic amine, heterocyclic amine, etc. are mentioned. As said fatty amine, monomethylamine, dimethylamine, a trimethylamine, ethylamine, diethylamine, triethylamine, n propylamine, G n propylamine, tree n propylamine, isopropylamine, etc. are mentioned concretely. Moreover, as aromatic amine, benzylamine, an aniline, N-methylaniline, N,N-dimethylaniline, o-methylaniline, m-methylaniline, p-methylaniline, N,N-diethylaniline, a diphenylamine, a G p-tolyl amine, etc. are mentioned concretely. As heterocyclic amine, although a pyridine, o-methylpyridine, o-ethyl pyridine, 2, 3-lutidine, 4-ethyl-2-methylpyridine, 3-ethyl-4-methylpyridine, etc. are mentioned concretely, the amine of a low-boiling point, for example, monomethylamine, dimethylamine, a trimethylamine, ethylamine, diethylamine, and fatty amine like triethylamine are still more desirable by especially strong base nature. These may be used independently, and two or more sorts may be combined and they may be used.

[0062] Moreover, in addition to the - (C) component (above-mentioned [ A ]) or (A) - (D) component, (E) N and N-G alkyl carboxylic amide can be contained. An improvement of the configuration of the resist pattern isolated by containing the aforementioned (E) component can be performed. (E) The content of a component has 0.1 - 5% of the weight of the desirable range to the (A) component. As the aforementioned (E) component, N of low-grade carboxylic amide and N-G alkyl group substitution product are desirable, and N,N-dimethylformamide or N,N-dimethylacetamide is specifically mentioned. The aforementioned (E) component may be independent, or two or more sorts may be combined and it may be used.

[0063] Furthermore, it is good to blend an extinction agent. As said extinction agent, for example 1-[1-(4-hydroxyphenyl) isopropyl]-4-[1 and 1-bis(4-hydroxyphenyl) ethyl] benzene, The naphthoquinone -1 of polyphenol, such as a screw (4-hydroxy - 3, 5-dimethylphenyl) -3 and 4-dihydroxy phenylmethane, a 2-diazo-5-sulfonate, A benzophenone can be mentioned, and while excelling in sensibility and the improvement effectiveness of definition by blending these extinction agents, since it also has the operation which the effect of a standing wave is controlled, and a cross-section configuration does not become wavelike, but forms a rectangular resist pattern, it can be used preferably. It is blended in the range which does not exceed 30 % of the weight to the total quantity of the (A) component and the (B) component which were described above as loadings of this extinction agent, and is preferably blended in 0.5 - 15% of the weight of the range. Since a profile configuration will worsen if these loadings exceed 30 % of the weight, it is not desirable.

[0064] As for the positive-resist constituent containing each above-mentioned component, it is desirable to use in the form of the solution which dissolved in the solvent in the use. As an example of such a solvent, an acetone, a methyl ethyl ketone, a cyclohexanone, Ketones, such as methyl isoamyl ketone and 2-heptanone; Ethylene glycol, Ethylene glycol mono-acetate, diethylene-glycol, and diethylene-glycol mono-acetate, The monomethyl ether of propylene glycol and propylene glycol mono-acetate, dipropylene glycol, or dipropylene glycol mono-acetate, Polyhydric alcohol and the derivatives of those, such as the monoethyl ether, the monopropyl ether, the monobutyl ether, or the monophenyl ether; Ring type ether; and methyl lactate like dioxane, Ester, such as ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, pyruvic-acid



ethyl, methoxy methyl propionate, and ethoxy ethyl propionate, can be mentioned. These may be used independently, and two or more sorts may be mixed and they may be used.

[0065] Moreover, addition content of what is used [ surfactant / the additional resin for improving the engine performance of a positive-resist constituent and an additive with a miscibility, for example, the resist film, by request, the plasticizer, the stabilizer, the coloring agent ] commonly can be carried out.

[0066] Dissolve in a solvent and a spinner etc. is used for the above-mentioned positive-resist constituent. For example, the substrate which prepared insulator layers, such as a silicon wafer, a silicon nitride (SiN), and BPSG, After having been applied to the substrate which prepared metal membranes, such as titanium nitride (TiN), aluminum-Si-Cu, and a tungsten, drying and being formed in a sensitization layer, with a contraction projection aligner etc. [ whether deep-UV light and excimer laser light are irradiated through a desired mask pattern, and ] It draws with an electron ray, a development is carried out using a developer, for example, a weak alkaline water solution like a 1 - 10-% of the weight tetramethylammonium hydroxide water solution etc., and a resist pattern faithful to a mask pattern and good is formed. Thus, said positive-resist constituent can form the resist pattern which was excellent depending on various substrates.

[0067]

[Embodiment of the Invention] Next, although the example of manufacture and an example explain this invention to a detail further, this invention is not limited at all by these examples.

[0068] After having dissolved polyhydroxy styrene 120g of example of manufacture 1 weight average molecular weight 13,000, and a molecular weight distribution (Mw/Mn) 1.5 in 680g of N,N-dimethylacetamide, adding G tert-butyl-G carbonate 85.0g into this solution and dissolving completely with scrambling, it was dropped having triethylamine 59 bet it for about 15 minutes. It stirred as it is after dropping termination for about 3 hours. Subsequently, the pure water of an amount was added 20 times to the obtained solution, and the polyhydroxy styrene by which the hydroxyl group was permuted by the tert-butoxycarbonyloxy radical was deposited. This sludge was washed, dehydrated and dried with pure water, and polyhydroxy styrene (weight-average-molecular-weight 13,000, molecular weight distribution 1.5 (Mw/Mn)) 150g by which 39-mol% of the hydroxyl group was permuted by the tert-butoxycarbonyloxy radical was obtained.

[0069] After having dissolved polyhydroxy styrene 120g of example 1 weight average molecular weight 13,000 and a molecular weight distribution (Mw/Mn) 1.5 in 680g of N,N-dimethylacetamide, adding 1-chloro-1-ethoxy ethane 42.3g into this solution and dissolving completely with scrambling, it was dropped having triethylamine 78.8 bet it for about 30 minutes. It stirred as it is after dropping termination for about 3 hours. Subsequently, the pure water of an amount was added 20 times to the obtained solution, and the polyhydroxy styrene by which the hydroxyl group was permuted by the 1-ethoxy ethoxy radical was deposited. This sludge was washed, dehydrated and dried with pure water, and polyhydroxy styrene (weight-average-molecular-weight 13,000, molecular weight distribution 1.5 (Mw/Mn)) 130g by which 39-mol% of the hydroxyl group was permuted by the 1-ethoxy ethoxy radical was obtained.

[0070] Polyhydroxy styrene (weight-average-molecular-weight 13,000, molecular weight distribution 4.0 (Mw/Mn)) 150g by which 39-mol% of the hydroxyl group was permuted by the tert-butoxycarbonyloxy radical was obtained like the example 1 of manufacture except having replaced polyhydroxy styrene with weight average molecular weight 13,000 and the polyhydroxy styrene of a molecular weight distribution

(Mw/Mn) 4.0 in the example 1 of example of comparison manufacture 1 manufacture.

[0071] Polyhydroxy styrene (weight-average-molecular-weight 13,000, molecular weight distribution 4.0 (Mw/Mn)) 130g by which 39-mol% of the hydroxyl group was permuted by the 1-ethoxy ethoxy radical was obtained like the example 1 except having replaced polyhydroxy styrene with weight average molecular weight 13,000 and the polyhydroxy styrene of a molecular weight distribution (Mw/Mn) 4.0 in example of comparison manufacture 2 example 1.

[0072] Polyhydroxy styrene 3g obtained in the example 1 of example 2 manufacture, and polyhydroxy styrene 7g obtained in the example 1, Bis(cyclohexyl sulfonyl) diazomethane 0.4g, bis(2, 4-dimethylphenyl sulfonyl) diazomethane 0.1g, After dissolving pyrogalloltrimesylate 0.2g, 0.02g [ of salicylic acid ], and benzophenone 0.1g in propylene-glycol-monomethyl-ether acetate 45g, What filtered the solution which furthermore added triethylamine 0.03g and 0.5g of N,N-dimethylacetamide, and was obtained by dissolving with the membrane filter of 0.2 micrometers of apertures was prepared as coating liquid of a positive resist.

[0073] Next, the prepared coating liquid was applied on the silicon wafer using the spinner, on the hot plate, it dried for 90 seconds and 80 degrees C of resist film of 0.7 micrometers of thickness were obtained.

Contraction projection aligner NSR-2005EX8A (NIKON CORP. make) was used for this film, after applying and exposing 1 mJ of doses at a time, it heated for 90 seconds, and subsequently the development was carried out for 65 seconds at 23 degrees C with the tetramethylammonium hydroxide water solution 2.38% of the weight, it rinsed and dried for 30 seconds, and 105 degrees C of resist patterns were formed. The effect of a standing wave does not have the formed resist pattern cross section, it is a good thing near a rectangle, and 0.21-micrometer Rhine and a tooth-space pattern were formed. Moreover, as a result of measuring as sensibility the minimum light exposure in which patterning of the resist pattern of the large area which can be checked visually is carried out, and a substrate front face appears, it was 11 mJ/cm<sup>2</sup>. Furthermore, as a result of investigating the thermal resistance (temperature which the flow by heat produces) of the formed resist pattern, it was 135 degrees C. It was 2.0 micrometers when asked for the maximum width (micrometer) of the focus by which 0.25-micrometer Rhine and a tooth-space pattern are formed in 1:1 as depth of focus width of face. When this resist solution was saved at 25 degrees C among the brown bottle and preservation stability was investigated, there was no generating of a foreign matter for six months.

[0074] Moreover, when the time amount from the exposure in which a resist pattern is formed in like the above as stability with the passage of time every \*\*, and 0.25-micrometer Rhine and the tooth-space pattern of a profile configuration perpendicular [ a side face ] and good are formed to exposure afterbaking processing was measured, it was for 90 minutes.

[0075] After dissolving polyhydroxy styrene 3g obtained in the example 1 of example of comparison 1 comparison manufacture, polyhydroxy styrene 7g obtained in the example 2 of comparison manufacture, bis(cyclohexyl sulfonyl) diazomethane 0.7g, and 0.05g of salicylic acid in propylene-glycol-monomethyl-ether acetate 45g, what filtered the solution which added triethylamine 0.01g and 0.2g of N,N-dimethylacetamide further, and was obtained by dissolving with the membrane filter of 0.2 micrometers of apertures was prepared as coating liquid of a positive resist.

[0076] Next, the resist pattern was formed for the prepared coating liquid like the example 2. The effect of a standing wave does not have the formed resist pattern cross section, it is a good thing near a rectangle, and 0.21-micrometer Rhine and a tooth-space pattern were formed. Moreover, as a result of measuring as

sensibility the minimum light exposure in which patterning of the resist pattern of the large area which can be checked visually is carried out, and a substrate front face appears, it was 15 mJ/cm<sup>2</sup>. Furthermore, as a result of investigating the thermal resistance (temperature which the flow by heat produces) of the resist pattern of the large area which can be checked by formed viewing, it was 125 degrees C. It was 1.6 micrometers when asked for the maximum width (micrometer) of the focus by which 0.25-micrometer Rhine and a tooth-space pattern are formed in 1:1 as depth of focus width of face. When this resist solution was saved at 25 degrees C among the brown bottle and preservation stability was investigated, there was no generating of a foreign matter for six months.

[0077] Moreover, every \*\*, as stability with the passage of time, except having set exposure afterbaking processing as for 110 degrees C and 90 seconds, when the time amount from the exposure in which a resist pattern is formed in like an example 2, and 0.25-micrometer Rhine and the tooth-space pattern of a profile configuration perpendicular [ a side face ] and good are formed to exposure afterbaking processing was measured, it was for 60 minutes.

[0078] In example 3 example 2, the resist pattern was formed like the example 2 except having used the substrate as the silicon wafer with which the metal membrane of TiN was formed. The formed resist pattern cross section did not have the effect of a standing wave, it is a good thing near a rectangle and 0.23-micrometer Rhine and a tooth-space pattern were formed.

[0079] In example 4 example 2, the resist pattern was formed like the example 2 except having used the substrate as the silicon wafer with which the insulator layer of BPSG was formed. The formed resist pattern cross section did not have the effect of a standing wave, it is a good thing near a rectangle and 0.23-micrometer Rhine and a tooth-space pattern were formed.

[0080]

[Effect of the Invention] The base material resin for positives resist of this invention is useful as a resinous principle of a chemistry magnification mold positive-resist constituent, and it is high sensitivity, and while having the high definition below a quarter micron and excelling in stability with the passage of time and the preservation stability of a resist solution thermal resistance, a depth of focus width-of-face property, and every \*\*, the resist constituent which can form the resist pattern which does not have a substrate dependency and was excellent in the profile configuration can be manufactured.

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[Translation done.]